International Journal of Thermophysics, Vol. 5, No. 1, 1984

Present Status of Research on Radiative Properties of Materials

T. Kunitomo[1]

Received February 8, 1984

Thermal radiative properties of materials, exclusive of spectroscopic properties in the vacuum ultraviolet, ultraviolet, and visible regions, are discussed. Previous results at both high and low temperatures are evaluated. Inorganic and organic materials as pure gases, flames, liquids, pure metals, and alloys are included, with regard to their spectroscopic and integrated properties. Experimental data and techniques and theoretical treatments are explained using typical examples. The interpolation and extrapolation methods using a limited number of experimental data are briefly explained.

KEY WORDS: alloys; gases; liquids; metals; optical constants; organic materials; spectroscopic properties; thermal radiative properties.

1. INTRODUCTION

Thermal radiative properties of materials are necessary to calculate heat transfer and to discuss thermal structure in energetic and thermal design of systems for scientific and engineering purposes both under high and low temperatures. In the cases of other thermophysical properties, such as thermal conductivity, thermal diffusivity, and specific heat, many measuring techniques have been proposed, and the proper techniques are established from the viewpoints of simplicity and exactness. In those cases where experimental errors can be evaluated precisely and fairly, exact experimental values have been presented both graphically and in tables. However, in the case of thermal radiative properties, exact experimental methods have not been established, and large errors are included in the published data.

Presented at the Japan–United States Joint Seminar on Thermophysical Properties, October 24–26, 1983, Tokyo, Japan.

[1]Department of Engineering Science, Faculty of Engineering, Kyoto University, Kyoto, Japan.

0195-928X/84/0300-0073$03.50/0

Further, the theoretical basis has been insufficient to extrapolate a limited number of experimental data to the unmeasured and broad temperature region. However, in the last ten years, marked progress has been realized on these problems by several researchers. In this paper, the present status of research on thermal radiative properties of gases, flames, liquids, pure metals, alloys, for both inorganic and organic substances, is discussed, and the current state of the art on the theoretical basis for treating the measured values of radiative properties of both fluids and solids is described briefly.

2. RADIATIVE PROPERTIES OF MATERIALS AND THEIR THEORETICAL TREATMENT

2.1. Gases

The gases whose radiative properties have been studied previously and correlated for practical use are H_2O, CO_2, NO, CO, SO_2, NH_3, CH_4, N_2O, HCl, HBr, HF, and air. The fundamental properties are classified into two groups, i.e., the narrow band model and the wide band model parameters [1, 2]. As to thermal data, the wide band parameters can be used more easily. However, for the measurements of temperature, concentration, etc., of gases, the spectral data are usually more useful. From the narrow band model parameters of the spectral absorption coefficient (S/d), the line shape parameter (γ/d), and the broadening coefficient (B, F), the spectral emissivity or absorptivity can be calculated as a function of temperature, pressure, and path length, where S is the line intensity, d is the line spacing, and γ is the line halfwidth. The exponential wide band model, which is generally used, is expressed by the following equations:

$$S/d(\omega^*) = (C_1/C_3) \cdot \exp(-\omega^*/C_3), \qquad \omega^* = |\omega - \omega_0|$$

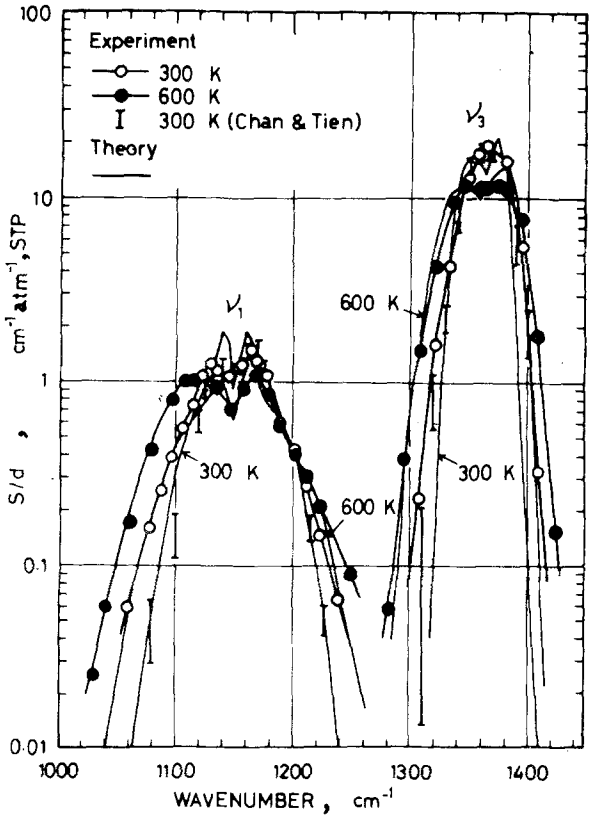
$$\gamma/d = C_2^2 Pe^n/(16 C_1 C_3) \tag{1}$$

$$Pe = P_B + BP_A$$

where ω_0 is the wavenumber of the band center. Three main parameters must be determined from the spectral data. The first is the integrated absorption coefficient C_1, the second is the line broadening parameter C_2, and the third is the band broadening parameter C_3, which is related to rotational constants of molecules. Pe is the effective pressure, and n is the pressure exponent. P_B and P_A are the pressure of broadening gas and that of absorbing gas, respectively. B is the self-broadening coefficient. From

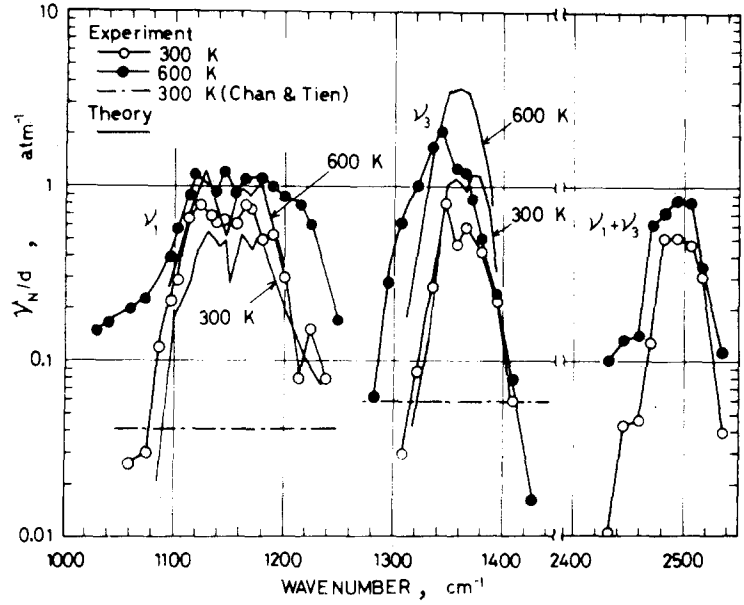
the wide band model parameters, the total emissivity or the total absorptivity can be easily calculated. The research on the narrow band and wide band model parameters has been carried out by Ludwig, Malkmus, Thomas, Ferriso, Tourin, Oppenheim, Varanasi, Tejwani, Goldman, Ben-Aryeh, Lowder, Tien, Chan, Burch, Howard, Williams, Edwards, Cess, Goldstein, Penner, Detkov, and others in various countries, and by Yamamoto, Tanaka, Kunitomo, Osumi, and others in Japan since the 1960s.

Examples of the spectral absorption coefficient, the lineshape parameters, and the self-broadening coefficients for the infrared bands of SO_2 are shown in Fig. 1(a–c). The wide band model parameters determined from these data are shown in Table I [3]. In previous studies, the three parameters of the narrow band model in a specific band were obtained indepen-



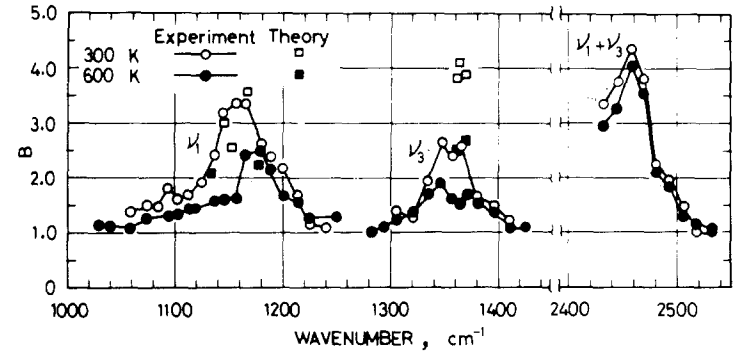
(a)

Fig. 1. (a) Absorption coefficients in the ν_1 and ν_3 bands of SO_2.



(b)

Fig. 1. (b) Lineshape parameters in the ν_1, ν_3, and $\nu_1 + \nu_3$ bands of SO_2.



(c)

Fig. 1. (c) Self-broadening coefficients in the ν_1, ν_3, and $\nu_1 + \nu_3$ bands of SO_2.

dently by different researchers. The author has developed a new method by which the three parameters can be determined simultaneously from a simple absorption experiment [4]. In this case agreement between experiment and theory is automatically assured. The total emissivities calculated by the wide band model parameters are shown for SO_2 in Fig. 2 [3]. The

Table I. Exponential Wide Band Model Parameters of Infrared Bands of Sulfur Dioxide.

Band	ω_0	C_1 $(cm^{-2} \cdot atm^{-1})$	C_2 $(cm^{-3/2} \cdot atm^{-1/2})$	C_3 (cm^{-1})	n	B
ν_1	1152	$113(300/T)$	200	$48(T/300)^{1/2}$	1.0	1.9
		$110(300/T)$	197	$48(T/300)^{1/2}$		
ν_2	519					
		$109.9(300/T)$				
ν_3	1361	$850(300/T)$	354	$20(T/300)^{1/2}$	1.0	1.9
$\nu_1+\nu_3$	2500	$15.6(300/T)\{\phi_1(T)/\phi_1(300)\}$	$61\{\phi_1(T)/\phi_1(300)\}^{1/2}$	$32(T/300)^{1/2}$	1.0	1.9
$2\nu_1$	2300	$2(300/T)\{\phi_2(T)/\phi_2(300)\}$	$27\{\phi_2(T)/\phi_2(300)\}^{1/2}$	$48(T/300)^{1/2}$	1.0	1.9
$\nu_2+\nu_3$	1876	$4.7(300/T)\{\phi_3(T)/\phi_3(300)\}$	$34\{\phi_3(T)/\phi_3(300)\}^{1/2}$	$34(T/300)^{1/2}$	1.0	1.9

revised values (solid lines) of the total emissivities are obtained very easily if the wide band model parameters are determined experimentally. The previous values of total emissivities of several gases are now being revised. In the past, the lineshape parameters and the broadening coefficients were treated as constants, but they are not constant and depend on temperature as shown in Fig. 1(b) and (c). In the application to temperature or concentration measurement, these variations must be considered. However, in the application to heat transfer calculation, they can be treated as constants since the error due to such an assumption is very small.

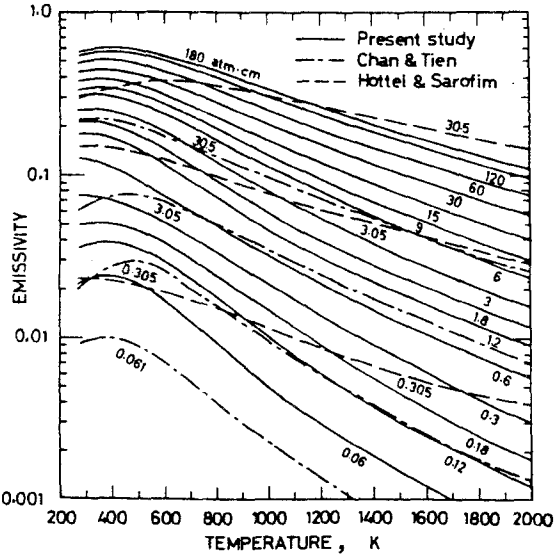


Fig. 2. Total gas emissivities of SO_2.

The collection and the correlation of the data are found in refs. [1] and [2]. Recommended values of emissivities or absorptivities of the gases described in these references can be found in ref. [5]. Using wide band model parameters, even the effect of coexistent infrared-inactive and infrared-active gases can be easily taken into consideration. The measuring technique adopted in previous studies is usually the transmission procedure, using an absorption cell, which works well, except the saturated region. The analytical method using the narrow band and the wide band models to obtain the parameters is also well established [4]. So if one wants to know the radiative properties of other gases not mentioned above, it is better to do an experimental study than to estimate the properties from those of similar gases.

Previous studies were mainly on gases or superheated vapors, and the radiative properties for their saturated states are lacking. The latter cases are considered to be much different from those of gases because of the existence of polymers as the association theory indicates. However, Lowder [6] and Kunitomo [7] have examined the effect of a dimer upon the integrated absorption coefficient of water vapor. The lack of such data is mainly due to the difficulty in making a transmission cell of saturated vapor. A very thin layer of condensed liquid at the cell window significantly affects the absorption properties, and the narrow band and wide band model parameters cannot be determined.

When calculating heat transfer in gases, the average absorption coefficient is usually used. However, at present, only the Planck mean absorption coefficient for very weak absorption and the Rosseland mean absorption coefficient for the very strong absorption of diffusion approximation are calculated. A simple method is needed to estimate the effective average absorption coefficient for the usual condition between very weak and very strong absorptions.

2.2. Liquids

Studies on radiative properties of various kinds of liquids are needed, particularly in heat transfer analysis in molten metal furnaces in the metal industry, in the solidification process of molten resin, in the absorption of solar energy in solar ponds, and in other systems. The radiative properties of molten metals are similar to those of their respective solids, but measurements at very high temperatures are very difficult and the experimental error becomes very large. Previously, the studies were carried out by a few physicists, Hodgsen, Shvarev, and others, and not by researchers in the engineering field. The wavelength region studied did not exceed 4 μm, and the dispersion equations of optical constants which can be applied in the

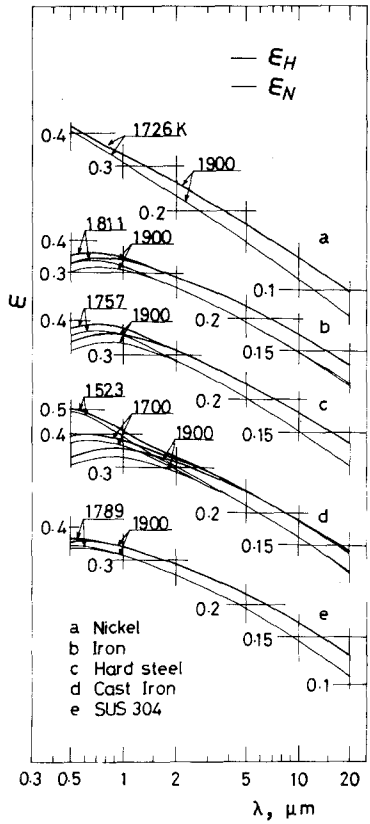


Fig. 3. Spectral emissivities of transition metals and alloys in the liquid state.

long wavelength region were not obtained; so their data cannot be applied to engineering calculations. Several data on spectral emissivities of simple metals are presented in ref. [5]. Recently, data on emissivities and dispersion parameters of several metals and alloys which can be used in the usual thermal calculations were given by Makino et al. [8]. Examples of the data of spectral and total emissivities are shown in Figs. 3 and 4. Almost all of the previous data as well as the present data were obtained for the condition of a fairly clean surface. Usually, the surface of a molten metal is easily contaminated, but the effect of contamination on its radiative properties has not been made clear and has not been treated quantitatively.

The absorption spectra in the infrared region of organic and inorganic liquids are collected in spectral data books for the assignment of matters but not adjusted for application to heat transfer calculations. The absorp-

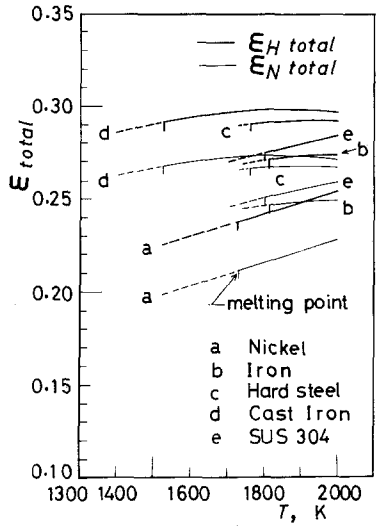


Fig. 4. Total emissivities of transition metals and alloys in the liquid state.

tion spectra of liquids, including scattering centers, will be crucial in some systems using solar energy, but they are lacking.

2.3. Flames

Usually, flames include infrared-active gases and several kinds of dispersed particles as sources of radiation. Although the data on gases in a flame are plentiful, as mentioned above, the data on the absorption and scattering by particles included are not adequate. In the case of flames resulting from burning diesel fuel oil and heavy oil, the effective absorption coefficients on the emissivities of the luminous flames were studied by Thring, Sarofim, Blokh, Kunitomo, Tien, and others, and good results for predicting the radiative properties were obtained.

However, the absorption coefficients or emissivities of coal burning flames have not been studied in detail, and variations of the radiative properties due to the change of coals to respective cokes, or due to chars and ashes in the flames have not been examined in detail. It is difficult to estimate the radiative properties since the shape of such particles is random (not spherical), and the correct values of the optical constants are not known. Reliable data are limited to the complex refractive indices at the wavelength 0.546 μm, and these are mainly used for the assignment of chemical composition. The difficulty of obtaining the exact values of optical constants of coals and cokes is caused by the fact that optically smooth surfaces of these materials for reflection measurements cannot be

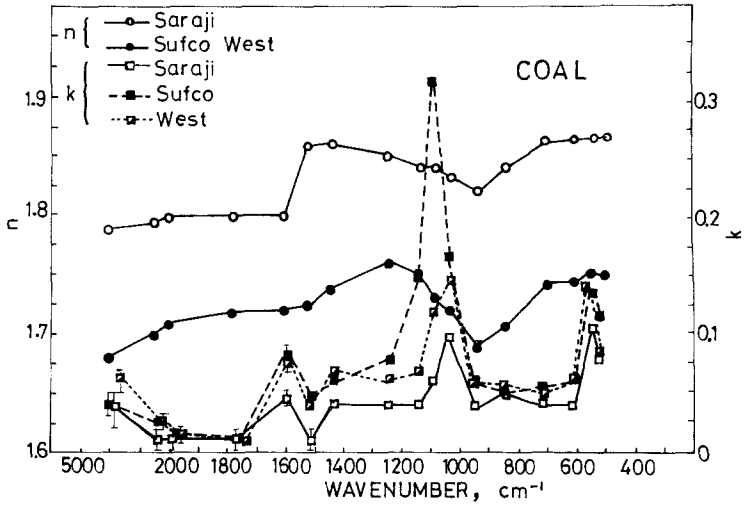


Fig. 5. Real and imaginary refractive indices of coal (particle extinction technique).

easily obtained, and similarly, neither can spherical particles for scattering measurements be obtained.

The author used the particle extinction technique and the dispersion formula to obtain the optical constants of coals and cokes, considering the particles to be spherical. Examples of the results by Brewster and Kunitomo [9] are shown in Figs. 5, 6, and 7. The carbon content of the

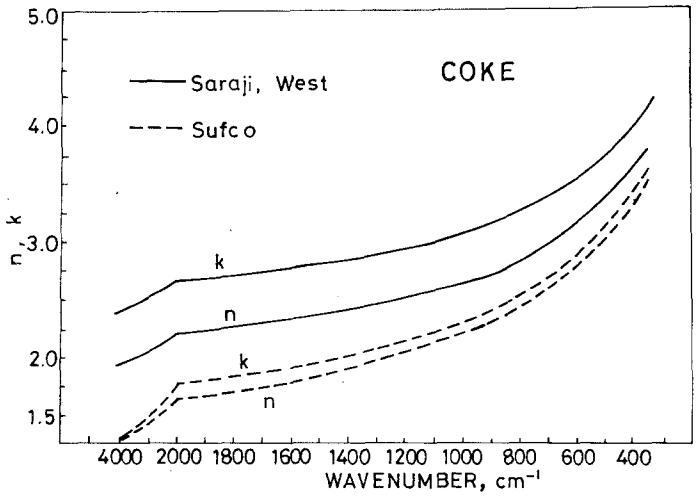


Fig. 6. Optical constants of coke (particle extinction technique).

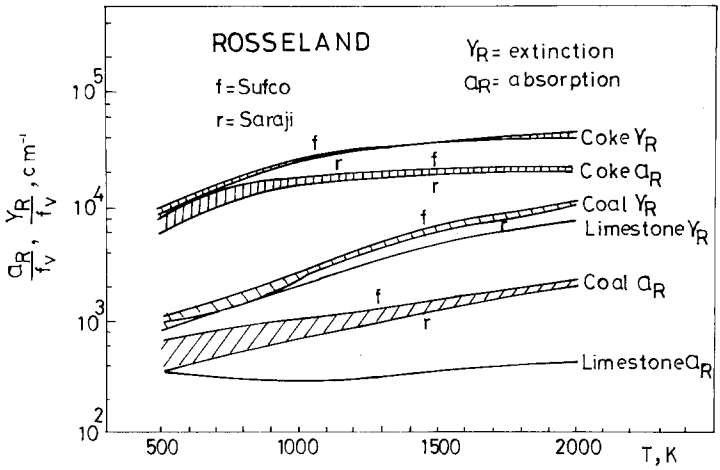


Fig. 7. Rosseland absorption and extinction coefficients of coal, coke, and limestone (d = 1 μm).

coals are 80~90% (Saraji coal), 70~80% (West coal), and 60~70% (Sufco coal). In Fig. 7, Rosseland absorption and extinction coefficients are shown, as well as those of limestone particles (d = 1 μm), which are used in fluidized-bed combustors. In these three figures, the values of coke particles are much different from those of coal particles.

2.4. Metals and Alloys

Regarding the optical properties of very familiar pure metals, many studies have been carried out, mainly at room temperature on clean specular surfaces. A large amount of data are collected and correlated in refs. [10] and [11]. For the radiative properties of high temperatures of common pure metals and those of alloys, the number of papers drastically decreases, but reliable data have been obtained by Price, Mard, Shvarev, Sevan, Makino, Kunitomo, and others on several kinds of metals and alloys. The data on heat resisting metals and alloys are especially lacking. An example of recent research carried out by Makino et al. [12] is shown in Fig. 8. These values were obtained by measurements and theoretical predictions.

The study of radiative properties at low temperatures is usually very difficult; the properties of some substances were measured by Toscano, Cravalho, Tien, Padalka, Biondi, Bos, Cunnington, Tsujimoto, Kunitomo, and others. An example of the research carried out by Tsujimoto et al. [13] is shown in Fig. 9. Studies to date have mainly treated specular surfaces;

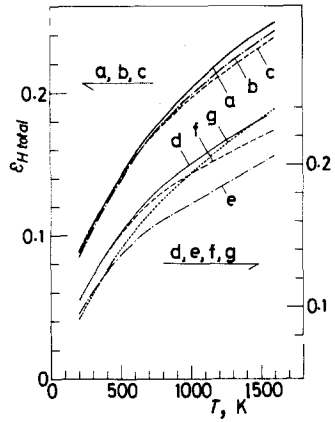


Fig. 8. Total emissivities of heat resisting alloys at high temperatures: (a) JIS SUS 304; (b) JIS SUS 316; (c) Incoloy 800; (d) Hastelloy x; (e) Inconel 600; (f) Inconel 617; (g) x-40.

radiative properties change significantly depending on the nature of the surface (e.g., surfaces produced by cutting, grinding, shotblasting, and hairline finishing) and on the surface contamination. The effects of various kinds of surface finishing and contamination should be studied quantitatively and correlations established for practical use.

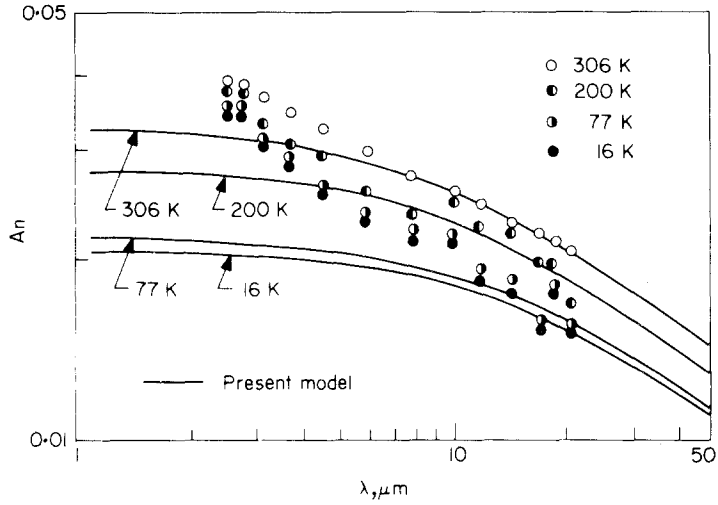


Fig. 9. Spectral normal absorptivity of Al alloys 2024(B); circles are the data and solid lines are the calculated values from the present model.

The relation between radiative properties and electric dc conductivities should be reexamined, especially for the prediction of the properties at extremely low and high temperatures where performance of experimental studies is very difficult. Such attempts were successfully carried out by the author [13] both at low and high temperatures by introducing the additional scattering term of conduction electrons into the optical dc conductivity in the dispersion formula of optical constants as

$$1/\tau_0 = 1/\tau_{dc} + 1/\tau_s \tag{2}$$

where τ_0 is the optical relaxation time, τ_{dc} is the electrical relaxation time, and $1/\tau_s$ is the term of the additional scattering in the surface layer. The idea is very simple: the optical collision frequency of the conduction electron is expressed by summation of the electric collision frequency and the additional collision frequency due to the specific disorder at the surface layer. The dispersion of the optical constants $\tilde{n}$ of a common metal is described by the contributions of two kinds of conduction electrons and one kind of bound electron as shown in the following equation [13]:

$$\tilde{n}^2 = 1 + \frac{S\lambda^2}{\lambda^2 - \lambda_0^2 + i\delta\lambda_0\lambda} - \frac{\lambda^2}{2\pi c \in_0} \sum_{k=1}^{2} \frac{\sigma_k}{\lambda_k - i\lambda} \tag{3}$$

where S (oscillation intensity), λ_0 (resonance wavelength), and δ (damping parameter) are parameters for a broad interband transition, and σ_k (optical dc conductivity) and λ_k (relaxation wavelength) ($k = 1, 2$) are parameters for absorption by conduction electrons at an anisotropic Fermi surface. The optical dc conductivity $\sigma_0 = Ne^2\tau_0/m^*$ is calculated by

$$\sigma_0 = \sigma_1 + \sigma_2 \tag{4}$$

where N is the number density of the conduction electrons, e is electron charge, and m^* is the effective mass of a conduction electron. The additional scattering affects only the behavior of a conduction electrons, which control the radiative properties in the longer wavelength region. This additional collision frequency can be determined easily from the electric dc conductivity and the spectral reflectivity data at room temperature [14].

By using τ_0, the radiative properties can be predicted, and the results are shown by solid lines in Fig. 9. In the analysis of the data given in the figure, the contribution of bound electrons was not taken into consideration because of the extremely low temperature, so large differences are found

between the experimental and theoretical values in the short wavelength region. If the contribution of bound electrons is considered, good agreement will be easily obtained. The effect of the additional scattering on the optical dc conductivity or on the optical resistivity is shown in Fig. 10 [12] and Fig. 11 [13] for high and low temperatures, respectively. The difference between the electric and optical dc conductivity is explained by the

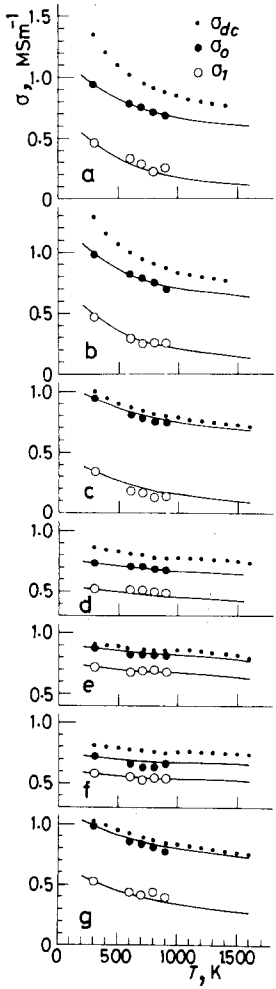


Fig. 10. Electric and optical dc conductivities of heat resisting alloys at high temperatures (symbols are the same as in Fig. 8).

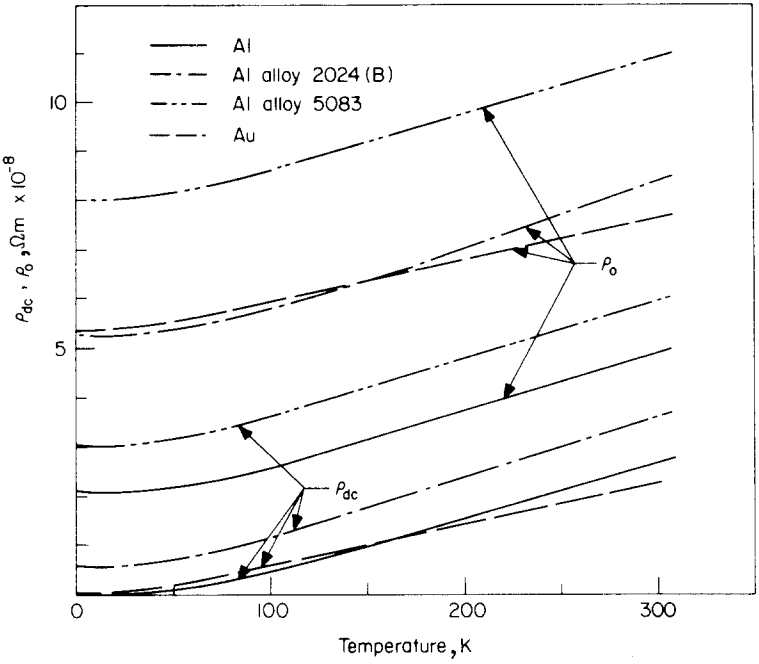


Fig. 11. Optical resistivities (calculated by the present model) and electrical resistivities.

constant value of additional collision and is not affected by temperature. σ_1 is the contribution of the first kind of conduction electrons. The electronic parameters determined to describe the behavior of the optical constants can be used in the wide temperature region if the transformation point is not included in the region. In the special case, the hysteresis phenomenon was found about the spectral emissivity. If hysteresis is found in the data on electric dc conductivity, the radiative properties also show the phenomenon. In conclusion, the emissivity or the reflectivity (both spectral and total) at a specified temperature T can be estimated from the emissivity or the reflectivity at room temperature and the electric dc conductivities at room temperature and at the temperature T.

2.5. Inorganic and Organic Materials

In the case of inorganic materials, we need to know the radiative properties of heat resisting and insulation materials at high temperatures and those of building materials at room temperature. As heat resisting materials, bricks and ceramics are very important. Macroscopic properties

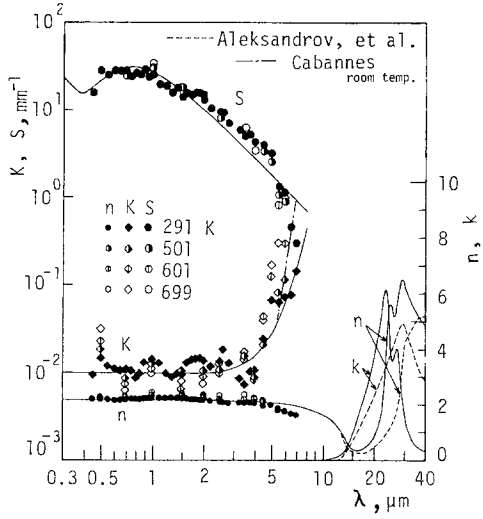


Fig. 12. Optical constants, absorption coefficients, and scattering coefficients of ZrO_2.

of bricks are usually similar in the infrared region and are collected in books on heat transfer. But the properties of ceramics, and especially of ceramic coatings, have not been studied well. They should be treated as semitransparent, scattering, and absorbing media. In previous measurements, this characteristics feature has not been taken into consideration. The interaction between ceramic and substrate must be considered, and this has been treated by the author. Examples of the spectral refractive index, the absorption coefficient, and scattering coefficient for ZrO_2 are shown in Fig. 12 [15]. From such data, the total hemispherical emissivities can be calculated as shown in Fig. 13 [15]. Fibrous insulation materials are also semitransparent, scattering-absorbing media, and were treated by Hasegawa et al. [16]. Regarding both common heat resisting and insulation materials, the experimental data should be adjusted to be applied easily to engineering calculations.

Regarding organic materials (synthetic resins, paint coating, timbers, cloth materials, the human body, and others) and inorganic materials (stones, concretes, etc.), one can find a few spectroscopic researches, among which the experimental and theoretical treatment proposed by Shafey and Kunitomo [17, 18] may be recommended. For example, the spectral diffuse and specular reflectances of the many kinds of timber surfaces obtained by Kunitomo and Sahashi [19] are shown in Fig. 14. This figure shows the characteristic feature of high diffuse reflectance of organic materials in the

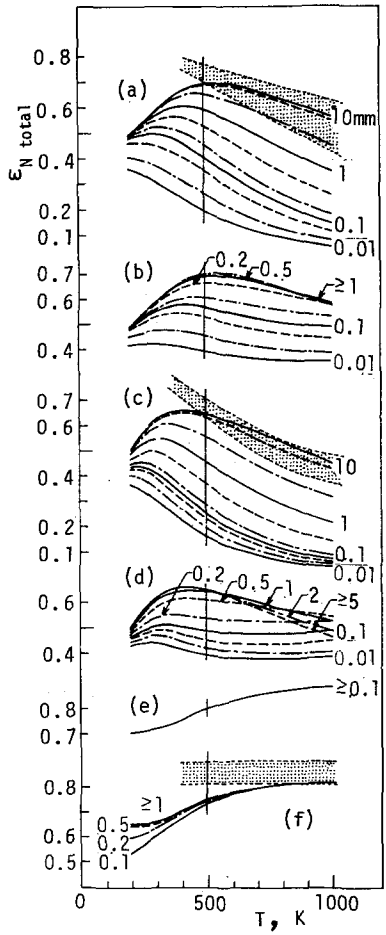


Fig. 13. Total normal emittances of several ceramics and ceramic coatings. (a) Al_2O_3; (b) Al_2O_3-Hastelloy X; (c) ZrO_2; (d) ZrO_2-Hastelloy X; (e) Si_3N_4; (f) SiC.

visible region. In the case of semitransparent scattering-absorbing media, special considerations must be taken into account. One is the effect of scattering and absorption inside the specimen. One-dimensionality about the radiative transfer must be assured in the measurement. On the problem of one-dimensionality, the study of Crosbie and Koewing [20] is recommended. Furthermore, semitransparent materials usually have complex spectral properties due to characteristic band absorptions and scattering, which depend on the size of the scattering center and the wavelength, as

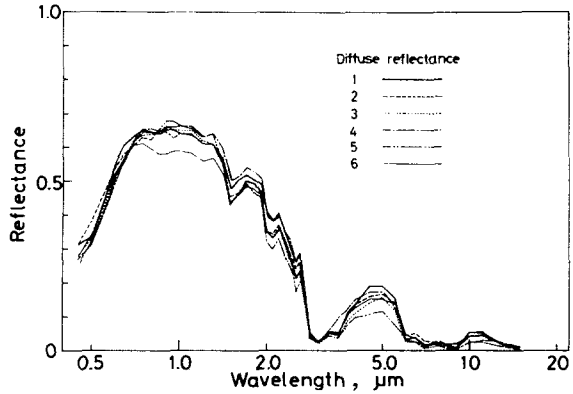


Fig. 14. Diffuse reflectance of timber surfaces: (1) *Chamaecyparis obtusa* (Japanese cypress); (2) *Tsuga canadensis* (hemlock); (3) *Chamaecyparis lawsoniana* (sun tree); (4) *Tilia* spp. (Japanese linden); (5) *Fagus drenata* (beach tree); (6) *Dicea* spp. (spruce).

shown in Fig. 12. So the spectral measurement is recommended rather than the total measurement since the measured properties in the former case can be applied more easily to extend the data.

REFERENCES

In the references section, only the main reference papers and handbooks or review books are listed since the citation of individual papers would have greatly lengthened and complicated this presentation.

1. C. B. Ludwig, et al., *NASA SP-3080, Handbook of Infrared Radiation from Combustion Gases* (NASA, Washington, D.C., 1973).
2. T. Kunitomo, *Developments in Heat Transfer, Vol. 2, Thermal Radiation of Gases and Flames* (Yokendo, Tokyo, 1974).
3. T. Kunitomo, H. Masuzaki, S. Ueoka, and M. Osumi, *J. Quant. Spectrosc. Radiat. Transfer* **25**:345 (1981).
4. T. Kunitomo and M. Osumi, *J. Quant. Spectrosc. Radiat. Transfer* **15**:345 (1975).
5. *JSME Data Book: Thermophysical Properties of Fluids*, chap. 4 (JSME, Tokyo, 1983).
6. J. E. Lowder, *J. Quant. Spectrosc. Radiat. Transfer* **11**:153 (1971).
7. T. Kunitomo, E. Ozaki, and K. Kawahara, *Heat Transfer Jpn. Res.* **11**:90 (1982).
8. T. Makino, H. Hasegawa, Y. Narumiya, S. Matsuda, and T. Kunitomo, *Proc. 20th Jpn. Heat Transfer Symp.* (1983), pp. 415–417.
9. M. Q. Brewster and T. Kunitomo, *ASME-JSME Thermal Eng. Joint Conf. 1983* **4**:21 (1983).
10. Y. S. Touloukian and D. P. De Witt, eds. *Thermophysical Properties of Matter*, Vol. 7 (IFI/Plenum, New York, 1970).
11. K. Kudo, ed. *Fundamental Thermophysical (Optical) Properties* (Kyoritsushuppan, Tokyo, 1972).
12. T. Makino, T. Kunitomo, and T. Mori, *Trans. JSME* **49**:1040 (1983).

13. S. Tsujimoto, M. Kanda, and T. Kunitomo, *Cyrogenics*, **22**:591 (1982).
14. T. Kunitomo and S. Tsujimoto, *Heat Transfer 1982 (Proc. 7th Int. Heat Transfer Conf.)* **2**:517 (1982).
15. T. Makino, et al., *Proc. 19th Jpn. Heat Transfer Symp.* (1982), pp. 265–267.
16. I. Kinoshita, K. Kamiuto, and S. Hasegawa, *Trans. JSME* **48B**:1520, (1982).
17. H. M. Shafey and T. Kunitomo, *Bull. JSME* **23**:1842 (1980).
18. H. M. Shafey, Y. Tsuboi, M. Fujita, T. Makino, and T. Kunitomo, *AIAA J.* **20**:1747 (1982).
19. T. Kunitomo and M. Sahashi, *Third Japan Symp. Thermophys. Prop.* (1982), pp. 117–120.
20. A. L. Crosbie and J. W. Koewing, *J. Quant. Spectrosc. Radiat. Transfer* **21**:573 (1979).